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SHORT COMMUNICATION

Color and chemical characterization of partially black-streaked heartwood in teak (*Tectona grandis*)

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Abstract: The heartwood of teak in certain areas of Java Island displays irregular black streaks along the annual rings. We investigated the color and chemical characteristics in a radial direction of partially black-streaked heartwood samples. Color properties (pH value, inorganic element, extractive content and extractive characterization) were measured in the color co-ordinates CIELAB system. The results show that the black streak part was 12-15 brightness (L*) value units less than the normal heartwood. Furthermore, the black streak part had more red (a*) but less yellow (b*), hue (h) and chroma (C*) than the normal wood. The pH value, ash content and calcium contents of the black streak part were slightly higher than those obtained for the normal wood. The content of the low-polar extractive (*n*-hexane and ethyl acetate) of the black streak part was considerably higher than that for the normal wood. The blackening process was speculated to be a kind of defense mechanism indicated by remarkable amount of bioactive compound called tectoquinone.

Keywords: *Tectona grandis*; black streak; extractives; inorganic materials

Introduction

Teakwood, harvested mostly from the island of Java, is the most valuable timber in Indonesia. By nature, teak heartwood is greyish-brown to dark golden brown in color. However, stems with an irregular black streak zone are frequently observed. This phenomenon is locally known as "doreng" which means streak. This blackening is known to occur only in the heartwood during a tree growing periods. The streak generally follows the annual ring in transversal section. This discoloration is categorized as a defect by some wood industries; thus it can degrade the timber quality. Forestry workers found that, from their experience, teak timber with black streaked wood depends on site conditions. It has been observed that the occurrence rate of black streaked progenies is in the black calcareous soil higher than that in the volcanic ash soil (Suhaendi 1998).

Shigo (1976) observed that discolorations in the living tree are mainly initiated through wounds, dying branches and roots. The natural blackening in the heartwood part has been studied in some species such as *Cryptomeria japonica* (Takahashi 1996; Kubo and Ataka 1998), *Diospyros celebica* (Noda et al. 2002; Minato and Morita 2005), and *Pycnanthus angolensis* (Starck et al. 1984). Those studies revealed that blackening is related to the chemical properties in the heartwood. Studies on relationship between wood color and chemical characteristics in teak are very limited. Thus, little information exists about the properties and development of black streaked wood in teak. The main purpose of this study was to investigate the color and chemical characteristics of wood with a partial black streak. The main parameters are pH value, inorganic element, extractive content as well as extractive analysis. The color characteristics were examined using CIELAB color specification.

Materials and methods

Sample preparation

A 32-year-old black streaked tree was felled at 28-cm diameter breast-height in the Perhutani Plantantion, Randublatung, Central Java Province. A disk in 5-cm thickness was taken at a height of 2 m above ground. In the disk, the black streak was located symmetrically around the outer heartwood. The wood sample was divided into four parts from sapwood to heartwood, then sampled correspondent part as SW, BH, NH-1, and NH-2, respectively (Fig. 1). Wood from each part (*ca.* 1.5 cm wide) from two opposite radii were converted into wood powder (40-60 mesh) and were then combined to form a single sample for further analysis.

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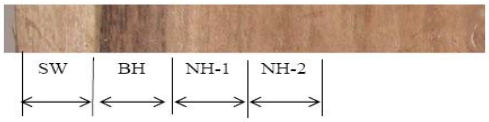

Fig. 1 Sampling position on a cross section of partially black-streaked heartwood in teak. SW = sapwood, BH = black streaked heartwood, NH = normal heartwood.

Color measurement

Wood color was measured on the air-dried wood powder using an NF777 spectrocolorimeter (Nippon Denshoku Ind. Co Ltd.) with an opening diameter of 6.0 mm. CIE standard illuminant A and a tungsten halogen light source were used. Percentage of reflectance data was collected at 20-nm intervals over the visible spectrum (400–700 nm). Three measurements were made for each part. The value L* describes psychometric lightness (0=black to 100=white). The value *a** represents a color parameter on the red/green axis; a positive *a** value represents red color, whereas a negative *a** value represents green color. The value *b** represents a color parameter on the yellow/blue axis; a positive *b** value represents yellow color, whereas a negative *b** value represents blue color. Combined, the values a* and b* define the hue (h) and chroma or saturation (C*). The h value (in angle) was calculated based on the equation h = arctg (b*/a*). C* was calculated using the equation $C^* = [(a^*)^2 + (b^*)^2]^{½}$.

Measurement of pH value

Wood powder (1 g per part) was extracted overnight in distilled water (20 mL) and then the pH of the filtrate was measured with a pH meter (Horiba). Three measurements were made for each part.

Inorganic elements analysis

Measurement of ash content was conducted according to the ASTM D-1102-1981 standard method. Wood powder samples (0.2 g) were prepared for elements analysis using a nitric acid-perchloric acid (5:3, v/v) solution with a digestion procedure. Measurements of potassium (K), calcium (Ca), magnesium (Mg) and iron (Fe) were carried out using a Hitachi Z-5000 atomic absorption spectrophotometer.

Determination of extractive content

Wood powder (2 g) was successively extracted with *n*-hexane, ethyl acetate (EtOAc), and methanol (MeOH) about 6 h for each in Soxhlet extractors. Extractions were carried out with 150 mL of each solvent and the refluxing times were kept at 5-6 times per hour. Cold-water and hot-water extractive content determinations were carried out according to ASTM D-1110 -1981 standard method.

Characterization of extractives

Thin layer chromatography (TLC) analysis

The extracts of *n*-hexane, EtOAc, and MeOH were applied to a thin layer chromatogram-plate silica gel 60 (Merck GF_{254}). The solvent used was benzene/ethyl acetate/acetic acid (18:2:1, v/v/v). Vanillin-sulphuric acid spraying was performed as a color test.

GC and GC-MS analysis

The extracts of *n*-hexane, EtOAc, and MeOH (concentration of 100 mg/mL) were analyzed using a Hitachi G-3500 GC equipped with FID and NB-1 capillary 30-m column. Operation temperature was 120–300ºC with a heating rate of 4ºC /min and held at 300ºC for 15 min. Injector and detector temperatures were set at 250ºC. Helium was used as the carrier gas, the split ratio was 80:1, and the injected volume was 1.0 μL. For quantification of individual substances, calibrations were made using known amounts of standard tectoquinone (2-methyl antahraquinone). Mass spectrometry measurements were obtained from GC-MS analysis on a Shimadzu QP-5000 with operation conditions being similar to GC analysis. The MS operating parameters were temperature ionization voltage of 70 eV, transfer line temperature at 250ºC, and scan range of 50–500 atomic mass unit.

The identification of the constituents was based on the comparison of retention data and mass spectra with those of the standards. The following reference samples were used: tectoquinone (25753-31 Kanto Chemical), lapachol (142905 Sigma-Aldrich), 2-hydroxymethyl anthraquinone (17241-59-7 Acros Organics), squalene (37309-30 Kanto Chemical), and palmitic acid (32016-30 Kanto Chemical). Deoxylapachol or its isomer (Windeisen et al. 2003) and tectol were identified by comparison of their mass spectra with those from previous studies by Lemos et al. (1999) and Perry et al. (1991).

Results and discussion

Measurement of color, pH and inorganic element

The results about color, pH and inorganic element measurements are summarized in Table 1. As expected, the discolored area was considerably darker in color. The discolored area had lower brightness (L*) values (12-15 units) compared with that in normal heartwood. The black streak had a more red value (a*) than sapwood and normal heartwood. Besides, it showed lower yellowness (b*), hue (h), and chroma (C*) values than sapwood and normal heartwood.

All pH values in the radial direction were in the weakly acidic range. The pH value of black streak was slightly higher than that of sapwood and normal heartwood. For some wood species, discoloration of wood has possibly been influenced by pH value (Sandermann and Rothkamm 1959). This may also be applicable to teak, although this result indicates that the discoloration process does not involve a comparatively large gradient of pH such as observed results in *C. japonica* (Takahashi 1996) or in *Pycnanthus angolensis* (Starck et al. 1984).

Previous reports on other species showed that inorganic elements in wood could be correlated with the blackening process in heartwood (Kubo and Ataka 1998; Minato and Morita 2005). The measurement of inorganic elements shows that the discolored tissue contains lower contents of K and Mg, but higher contents of Ca and Fe than those in the sapwood. The differences in inorganic levels between black streaked and normal heartwood

were less striking; however, a slightly higher amounts of Ca in the black streak part was noticeable. Of the four metal elements observed in the discolored part, the Ca level was the highest.

Table 1. The color, inorganic elements and pH value in the different wood parts

Parameters	Radial part			
	SW	BH	NH-1	NH-2
Color properties				
L* (brightness)	70.06	42.62	57.42	54.22
a* (redness)	3.81	7.45	6.60	6.28
b* (yellowness)	26.39	20.30	24.87	23.52
Hue (h, angle)	81.78	69.85	75.14	75.05
Chroma (C*)	26.66	21.62	25.73	24.34
Inorganic elements content				
Ash (%)	0.84	0.88	0.72	0.52
Potassium(ppm)	1950	810	880	880
Magnesium (ppm)	460	300	290	300
Calcium (ppm)	760	2500	1830	1740
Iron (ppm)	33	55	50	30
pH value	5.25	5.63	5.33	5.26

Notes: SW = sapwood, BH = black streaked heartwood, NH = normal heartwood.

Determination of extractives content

It is generally assumed that the darker heartwood contains more extractives. In this study, the extractive contents were appreciably higher in the black streak portion, particularly, in the low-polar soluble extracts (Table 2). The relatively high level of *n*-hexane extractive content in the heartwood is probably due to the age of the sample in this experiment (32 years). Earlier reports on teak showed that the heartwood of 30- year-old trees (Lukmandaru and Takahashi 2008) and 62-year-old trees (Narayanamurti et al. 1962) contained higher levels of apolar extractive content, compared to that in younger trees. The yields of cold-water and hot-water solubility did not differ substantially between the black streak and normal heartwood. The cold-water and hot-water solubility value in the black streak part was lower than that of the sapwood.

Table 2. The extractive content in the different wood parts

Extractive content	Radial part			
(%)	SW	BH	NH-1	NH-2
n-hexane	2.26	5.97	4.07	3.31
Ethyl acetate	0.43	2.85	1.17	1.59
Methanol	3.15	3.38	1.95	2.60
Cold-water	3.82	1.74	1.25	1.38
Hot-water	4.84	2.65	2.38	2.62

Notes: SW = sapwood, BH = black streaked heartwood, NH = normal heartwood.

Characterization of the extractives

Thin layer chromatography (TLC) analysis

TLC of *n*-hexane, EtOAc and MeOH extracts showed that the four major spots in both sides (black streak and normal heartwood) were identical. Based on the results from co-chromatography with authentic samples and a reference (Sandermann and Dietrichs 1959), the three identified spots were tectoquinone, tectol and tecomaquinone (dehydrotectol). The unidentified spot was not reactive with vanillin-sulphuric acid reagent, indicating that this spot does not belong to terpenoid type compounds. Of the three extracts, TLC of MeOH of the black-streaked heartwood revealed a striking high condensation spot.

GC and GC-MS analysis

The results of GC analysis of *n*-hexane, EtOAc and MeOH extract revealed the same typical peaks. The identified major components (Fig. 2) were lapachol, tectoquinone, squalene, tectol, and desoxylapachol or its isomer. Tecomaquinone could not be detected by NB-1 column. Many similar components in black streaked and normal heartwood were observed, but in different amounts. The quantification of the major components is presented in Table 3. As expected, the component levels are lowest in the sapwood. Tectoquinone is the most abundant component in all fractions of black streak portion. The most striking differences between the black streak and normal heartwood were observed in the levels of tectoquinone and squalene. In the discolored part, tectoquinone was significantly higher whereas squalene content was lower, almost the same as that of the sapwood. However, this GC peak pattern is reversed for the normal heartwood. Moreover, an unknown compound (peak 5) and 2-hydroxymethyl anthraquinone were present at considerably higher concentrations in the discolored part. The concentration differences of other extractives were not as pronounced. These findings indicate that chemical formation of the quinones is occurring, which takes place faster than that of terpenes in the discolored part.

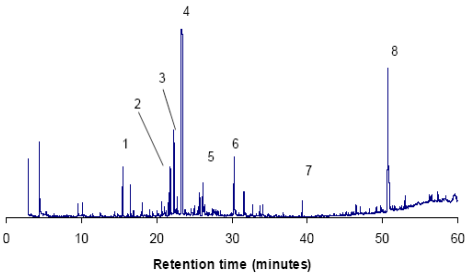

Fig. 2 Gas chromatogram of the *n*-hexane extract from black streaked heartwood in teak. (1.Desoxylapachol or its isomer; 2. Palmitic acid; 3. Lapachol; 4.Tectoquinone; 5. Unknown; 6. 2-hydroxymethyl anthraquinone; 7. Squalene; 8. Tectol).

In study on the blackening processes in the heartwood of *Diospyros kaki,* quinones are indicated as monomers of insoluble black substance (Yasue et al. 1975). Tectoquinone and 2-hydroxymethyl anthraquinone themselves are yellow and white, respectively. Both of these compounds, however, showed no change or darkening color in the TLC plates in an auto-oxidation test. It must be noted that the chromatographic system in this experiment was not able to detect the other soluble phenolic extractives responsible for the discoloration. Therefore, for a better explanation of the blackening mechanism, characterization and identification of the unidentified major compounds that were

found in the GC and TLC analysis need further research.

Table 3. The extractive components content in the different wood parts

Extractive components content	Radial part			
(%)	SW	BH	NH-1	NH-2
1. Desoxylapachol or its isomer	0.03	0.15	0.15	0.10
2. Palmitic acid	0.02	0.01	0.01	0.02
3. Lapachol	0.01	0.05	0.05	0.02
4. Tectoquinone	0.06	0.46	0.46	0.18
5. Unknown	0.08	0.29	0.02	0.16
6. 2-hydroxymethyl anthraquinone	0.04	0.22	0.04	0.03
7. Squalene	0.11	0.10	0.49	0.40
8. Tectol	0.04	0.32	0.24	0.22

Notes: SW = sapwood, BH = black streaked heartwood, NH = normal heartwood.

The role of tectoquinone in the natural durability of teak is recognized in several reports (Rudman et al. 1958; Sandermann and Simatupang 1966; Haupt et al. 2003). Although a direct bioassay test was not attempted in this study, it is suggested that the blackening processes may be related to some protective functions against other biological organisms. In this regard, teak may have similarity to *Diospyros kaki,* in which the black portion was more resistant to damaging organisms compared with that of the adjacent normal heartwood (Noda et al. 2002).

Conclusions

A comparison was made of color and chemical differences between sapwood, black-streaked heartwood and normal heartwood in teak. The black streak part had a more red (a*) value, but lower brightness (L*), yellowness (b*), hue (h) and chroma (C*) values than those in both sapwood and normal heartwood. The pH, ash and calcium levels of the black streak part were slightly higher than those of normal wood. Furthermore, this portion gave appreciably higher *n*-hexane and ethyl acetate extractive contents, compared to those in normal wood. GC and GC-MS analysis of *n*-hexane, ethyl acetate, and methanol extractives showed that the black streak heartwood contained significantly higher tectoquinone content but lower squalene content than that of normal heartwood. The conspicuously high level of tectoquinone suggests that the blackening of teak should be connected to a protective function.

The results are based on only one individual specimen; therefore, an additional larger number of samples are necessary to confirm differences between black streak and normal heartwood.

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